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Acoustic and Thermal Properties of Cerium Metaphosphate Glasses

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Abstract

To test predictions of the soft potential model for the acoustic and thermal properties of cerium metaphosphate glasses, the ultrasonic wave velocity and the thermal expansion have been measured as functions of temperature and pressure. The longitudinal ultrasonic wave velocities increase under pressure. The hydrostatic pressure derivative of the bulk modulus is positive: when compressed, these glasses show a normal elastic response. However, the pressure derivative of the shear modulus is negative and small, indicating weak softening of shear modes under pressure. The results found are used to determine the Grüneisen parameters, which are needed to obtain the acoustic mode contribution to thermal expansion. The temperature dependence of the shear wave ultrasound velocity, after subtraction of the relaxation and anharmonic contributions, follows a linear law as predicted by the Soft Potential Model.

Keywords - Metaphosphate glasses, acoustic, thermal expansion

1. Introduction

The distinctive acoustic vibrational, magnetic and magneto-optic phenomena are a feature of the rare earth glasses of composition in the vicinity of metaphosphate $(\text{R}_2\text{O}_3)_{0.25}(\text{P}_2\text{O}_5)_{0.75}$. Metaphosphate is a very stable composition, it is resistive to water: a valuable feature for device applications. These glasses find applications in the manufacture of magneto-optical devices, such as magnetically tunable lasers, amplifiers and frequency converters for the telecommunication industry [1]. Universality of the low-temperature and the low frequency anomalies in the dynamical properties of glasses suggests that their different aspects are interrelated and have the same microscopic origin [2]. Few models have been developed to describe the anomalous excess the density of states in the frequency range $<10 \text{ cm}^{-1}$. Most, if not all, anomalous properties can be accounted for by the Soft Potential Model (SPM) [3, 4]. This model can be regarded as an extension of the tunneling model, which explains the low-temperature properties for $T < 1\text{K}$, postulating the

existence of atoms, which can tunnel between two configurations of very similar energy. Recently, new approaches in the spirit of the SPM have been discussed [5].

The temperature and frequency dependences of the quasi-elastic scattering and Boson peak, using the analysis of the low-frequency Raman data, and the excess-mode specific heat at low temperature show general features, which are in qualitative agreement with the predictions of the SPM [6]. In addition the temperature dependence of the ultrasound velocity includes an excess contribution, which has linear temperature dependence; an observation that can also be accounted for within the framework of the SPM [7]. These excess excitations have also been shown to contribute to the thermal expansion and to the acoustic properties of La and Sm glasses [8]. Recently, the refractive index of can also be explained in terms of the glass thermal expansion [9]. To test the general applicability of the excess mode concept to other glasses, an acoustic and the thermal expansion studies have been made on cerium glasses as function of pressure and temperature. This work provides additional data of the vibrational properties of metaphosphate glasses.

2. Experimental Procedure

The glass samples containing cerium in concentration near the vicinity of the metaphosphate composition $(\text{Ce}_2\text{O}_3)_{0.25}(\text{P}_2\text{O}_5)_{0.75}$ were prepared from melts of mixtures of 99.9% purity grades of dry cerium oxide and phosphorous pentoxide, in an alumina crucible [10]. Cylindrical specimens of about 5 mm thickness were cut from the ingots and polished smoothly to produce flat faces parallel to within 10^{-3} radian. These glass samples are suitable for quantitative analysis and for the acoustic and thermal expansion measurements. Sample density was measured by Archimedes' method using toluene as the immersion liquid. Glass compositions were analyzed quantitatively by a JOEL JXA-8600M electron probe microanalyser.

The ultrasonic wave velocity and attenuation were measured as a function of temperature using the pulse-echo-overlap technique [11]. The changes in

ultrasonic wave velocity with pressure were measured under hydrostatic pressures, applied in a piston-and-cylinder apparatus sealed with O-rings and silicone oil was used as the pressure-transmitting medium. The thermal expansion was determined using a capacitance dilatometer capable of measuring length changes to within 0.02 Å of a sample having a length of 6 mm.

3. Results and Discussion

The temperature dependence of the attenuation of shear ultrasonic waves propagated in cerium metaphosphate glasses is dominated by a broad loss peak [12]. Excitations arising from thermally activated over potential barriers are considered to be the source of this broad attenuation peak, which is a characteristic feature of many oxide glasses [2]; analysis can be made assuming that it stems from thermally activated relaxation processes.

The relaxation parameters obtained from the attenuation data can now be used to evaluate the relaxation contribution to the temperature dependence of the ultrasonic wave velocity. Both longitudinal and shear ultrasonic wave velocities propagated in $(\text{Ce}_2\text{O}_3)_x(\text{P}_2\text{O}_5)_{1-x}$ glasses increase linearly with decreasing temperature down to about 100 K; below this temperature, the ultrasonic wave velocities increase more rapidly and this continues down to the lowest temperature reached. This temperature dependence of the ultrasonic wave velocity arises in part from anharmonic effect and from those of the thermally activated relaxations, which cause the peak in the ultrasonic attenuation [12]. The anharmonic contribution has been determined using an extension of the quasi-harmonic continuum model [7]. The calculated temperature dependence of the anharmonic contribution to the ultrasonic shear wave velocity is shown in Figure 1(a).

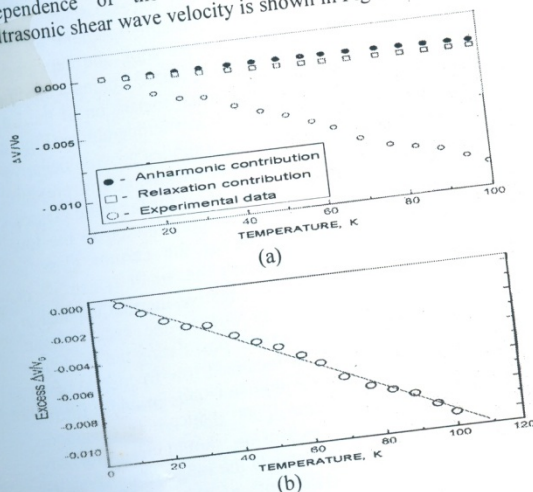


Figure 1: (a) The temperature dependence of the fractional velocity $\Delta V/V_0$ of shear ultrasonic waves propagated in $(\text{Ce}_2\text{O}_3)_{0.257}(\text{P}_2\text{O}_5)_{0.743}$ glass, (b) the contribution from the excess states.

When the sum of the anharmonic and relaxation contributions is subtracted from the experimentally determined velocity of shear ultrasonic waves as a function

follows a linear contribution from another mechanism. The dependence of the ultrasonic wave velocity on temperature range below 100 K (Figure 1(b)). This linear dependence of the excess velocity contribution found at low temperature for Cerium glass is in accord with this SPM prediction.

Application of hydrostatic pressure to Eu, Ho, Sm or Tb metaphosphate glasses [13-16] produces a decrease in ultrasonic wave velocity. The hydrostatic-pressure derivatives are negative: the application of pressure induces softening of the long-wavelength acoustic modes. Hence, the bulk modulus becomes larger as the pressure is increased. Cerium metaphosphate glasses, like those of La and Nd [17], become harder to squeeze under pressure. This is a normal elastic behavior under pressure.

Further physical insight into the acoustic vibrational behaviour of these glasses can be gained by investigating the anharmonicity of their long-wavelength acoustic modes. Measurements of the pressure dependences of the elastic stiffness can be used to quantify the vibrational anharmonicity of the low frequency modes by determining the acoustic-mode Grüneisen parameters, which measure the shift $-(\partial \ln \omega / \partial \ln V)$ of the long-wavelength acoustic mode frequency ω with volume V . For an isotropic solid there are two Grüneisen parameters, namely γ_L and γ_S for longitudinal and shear elastic waves, respectively.

In general, the mean acoustic-mode Grüneisen parameter γ^{el} in the long-wavelength limit must be obtained from γ_L and γ_S by use of complex weighing functions on the basis of Debye continuum model. The small positive values of γ_L obtained for each glass show that the application of hydrostatic pressure causes the longitudinal acoustic modes to stiffen slightly; this is a normal behavior in the sense that the mode energies are raised when the glass is squeezed volumetrically. However, the shear mode Grüneisen parameter γ_S is small and negative: the shear mode softens under pressure.

At low temperature the thermal expansion coefficient of each of the glasses becomes negative and shows an extremum located at negative values (Fig. 2) at about 13 K for $(\text{La}_2\text{O}_3)_{0.222}(\text{P}_2\text{O}_5)_{0.778}$, 16 K for $(\text{Ce}_2\text{O}_3)_{0.254}(\text{P}_2\text{O}_5)_{0.746}$ and 19 K for $(\text{Sm}_2\text{O}_3)_{0.248}(\text{P}_2\text{O}_5)_{0.752}$; the absolute value of α and the temperature range in which it is negative increases in that order.

The thermal expansion coefficients $\alpha(T)$ of these glasses are small. Both thermal expansion and pressure derivatives of the elastic stiffness from vibrational anharmonicity can be directly linked. Thermal expansion originates from the effect of anharmonicity terms in the potential energy. Using the partition function approach, it has been shown for a glass that the contributions of the acoustic mode vibrational anharmonicity to both thermal expansion and non-linear acoustic properties have the same sign [8]. In the quasi-harmonic approximation the thermal expansion parameter γ^{th} , a widely used measure of vibrational anharmonicity, is related to the volume thermal expansion α_V and specific heat C .

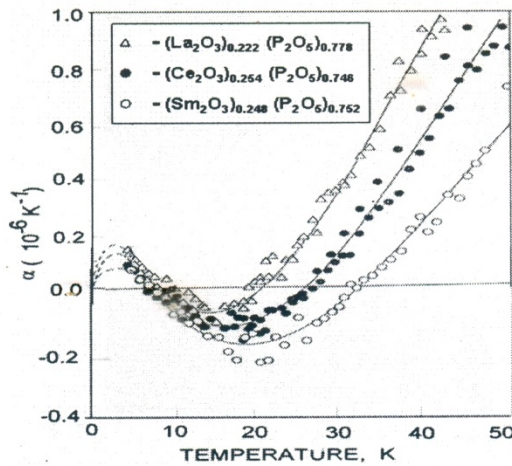


Figure 2: Temperature dependences below 50 K of the linear thermal expansion coefficients of La, Ce and Sm glasses.

The thermal Grüneisen parameter is the weighted average of all the individual mode Grüneisen parameters γ_i :

$$\gamma^{th} = \sum_i C_i \gamma_i / \sum_i C_i \quad (1)$$

Vibrational anharmonicity is also responsible for nonlinear acoustic properties. The contributions to thermal expansion from the acoustic phonons are determined by the mode Grüneisen parameters γ_L and γ_S , which are negative for the samarium metaphosphate glass and become more negative as the temperature is reduced below room temperature [15]. Since these acoustic modes have negative Grüneisen parameters, the thermal expansion is expected to be negative at low temperatures (Figure 2). In the case of lanthanum metaphosphate glass the acoustic-mode Grüneisen parameters are positive. Hence the acoustic phonon mode contribution to the thermal expansion at low temperatures should be positive. However the thermal expansion of lanthanum metaphosphate glass is also negative at low temperatures (Figure 2). In the case of the cerium metaphosphate glasses γ_L is small and positive: the acoustic phonon contribution to thermal expansion should be small. However as the temperature is lowered the longitudinal phonon population freezes out and the transverse phonons play a correspondingly larger role. The shear mode Grüneisen parameters of the cerium metaphosphate glasses are negative and so is the transverse phonon contribution to the thermal expansion. However the total anharmonic phonon contribution should be small and negative at low temperatures because γ^{el} is small and negative.

Since the thermal expansion of lanthanum metaphosphate glass is negative at low temperatures (Figure 2), like that of the samarium metaphosphate glass, although over a more restricted temperature range, it has been proposed [8] that there must be a contribution from the excess states which causes the negative incursion of the thermal expansion of lanthanum and samarium metaphosphate glasses in the low temperature regime. Expressions for the SPM contributions to thermal expansion and to nonlinear acoustic properties have been developed using a partition function approach and by

describing the quasi-local low-frequency modes in glasses by a soft anharmonic oscillator potential [3-5]

$$V(x) = \varepsilon \left[\eta \left(\frac{x}{a} \right)^2 + \xi \left(\frac{x}{a} \right)^3 + \left(\frac{x}{a} \right)^4 \right] \quad (2)$$

Here x is the generalised coordinate of the soft mode having units of length, a is a characteristic length of the order of the interatomic spacing, ε is the binding of the order of $mv^2 \approx 10\text{eV}$, m being the average mass of atoms making up the glass, v is the sound velocity. The dimensionless parameters η and ξ have random values due to fluctuations of the structural parameters of a glass and the soft potentials correspond to $|\eta|, |\xi| \ll 1$. The distribution function of the force constant η shows the so-called "sea-gull" singularity, as $|\eta| \rightarrow 0$, for a fixed value of ξ [4,5]. The contribution to the thermal expansion from the excess low-energy vibrational states has been shown [8] to be

$$\alpha_{SPM} = -\frac{3k_B \xi}{4\varepsilon \eta^2} \quad (3)$$

The contribution from the excess low-energy vibrational states to the pressure gradient for the elastic modulus M_{SPM} is

$$\left(\frac{dM}{dP} \right)_{SPM} = -\frac{6\varepsilon \xi}{a^3 M_{SPM}} \quad (4)$$

Hence, the contributions from the excess states to the thermal expansion and to the pressure gradient for the elastic modulus M_{SPM} have the same sign, and depend on the signs of the parameters ξ and ε ; where ε being a binding energy is positive. Since the thermal expansion of the La, Sm and Ce glasses are negative at low temperatures (Figure 2), ξ must be positive. The excess modes provide negative contributions to both the thermal expansion and pressure derivative of the elastic modulus M_{SPM} for these glasses. Although the anharmonic phonon contribution to the low temperature thermal expansion of the cerium glass is negative, its magnitude can only be small (since γ^{el} is negative and very small). The negative thermal expansion at low temperature is largely due to the excess mode contribution. Soft-potential model postulating the existence in glasses of the additional localized low-frequency (soft) modes besides the acoustic phonons. This provides further support for the suggestion [10] that an excess mode contribution to thermal expansion should occur for any vitreous materials, which extends the range of universality to the physical properties of a glass arising from topological disorder.

Although all these phosphate-based glasses have quite different structures, the observation that the soft harmonic oscillator relaxation contribution to the temperature dependence of ultrasonic wave velocity in these glasses is of similar magnitude is in accord with the proposal that the SPM should be universally applicable to glasses.

Conclusions

The ultrasonic wave velocity and thermal expansion of cerium metaphosphate glasses have been measured as a function of temperature and pressure. The results obtained provide a physical description of the vibrational anharmonicity of the glasses and are in agreement with predictions of the soft potential model (SPM).

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